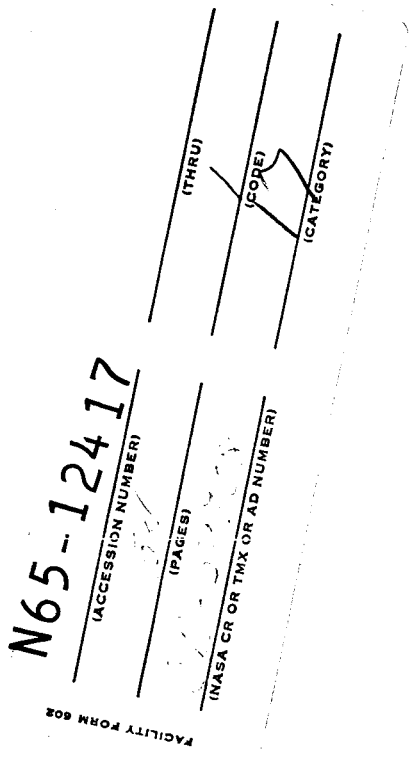
THE BOEING COMPANY
Aero-Space Division

IDENTIFYING OPTIMUM PARAMETERS OF HOT EXTRUSIONS

Contract NAS 7-276



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ABSTRACT

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The purpose of this program is to develop a technique for hot extruding MgO and to determine the effect of hot extrusion on MgO with preliminary evaluations on other oxide bodies. Approximately 50 ceramic billets have now been prepared, including MgO billets with less than 1% porosity fabricated without additives. Hot pressing of CeO_2 was unsuccessful in graphite dies, however, results indicate that Hastalloy B dies may prove successful in an air atmosphere and that isostatic pressing may also provide suitable CeO_2 billets.

Three extrusions in tungsten cans have been made. Several uncanned extrusions have been completed, however, a weighing of factors has lead to the selection of canned extrusion as the primary technique for the remainder of this program. Further evaluation of previous CaO extrusions showed that substantial recrystallization occurs after extrusion, however, no further recrystallization has been observed on annealing to 1370°C. Significant interaction of extrusion and alloying was shown by both redistribution of the CaO rich phase in MgO - 5 w/o CaO and greater orientation of phases in CaO - 14 w/o MgO, MgO - 1 w/o Al_2O_3, and MgO - 2 w/o NiO than in a similar pure MgO body.

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A. BILLET FABRICATION

1. MgO Billets

a. 1.5" Diameter Billets

Densities of 3.53 or above (less than 1% porosity) have been achieved in 6 out of 8 MgO billets without LiF as shown in Table I. The hot pressing procedure B employed, previously developed at Boeing for thinner specimens, is described in the Appendix.

These specimens were fired to 1565°C per Firing Schedule A of the Appendix, since firing to 1315°C on this same schedule left impurities as indicated by variations from translucent white appearances, especially in the Mallinckrodt MgO. The Mallinckrodt MgO also frequently showed excessive blistering, while little or no blistering was observed with the Fisher Electronic grade MgO.

Two billets of the same composition and fabrication parameters as billet A and two of the same as billet 2 of Table I of the Appendix were fabricated in graphite dies. The respective densities were approximately 2.6 gm/cc and 2.75 gm/cc. The specimens are for possible comparison with billets extruded without cans, and also to evaluate the effects of starting billet porosity on extruded billet porosity.

Eight MgO billets were hot pressed in graphite dies from Mallinckrodt MgO with 2% LiF per vacuum hot pressing procedure A of the Appendix. Their firing schedule and resultant densities are shown in Table I.

b. 3.0" Diameter Billets

A seventh MgO billet of approximately 3.0" in diameter was made the same as billet 4 of Table I of the Appendix, except that the hot pressing temperature was raised from 1600°C to 1900°C. This resulted in a higher density of 3.31 gm/cc (less than 8% porosity). Some adhesion due to reaction with the die (Graph-i-tite G) occurred, resulting in the corners of the billet breaking off. (This might be reduced by the use of graphite cloth on the ends of the rams if future billets are needed.)

2. MgO Alloy Billets

a. MgO-CaO

Four MgO - 4 w/o CaO* billets were fabricated in graphite dies without LiF per vacuum hot pressing Procedure B of the Appendix. Fisher MgO was mixed with the CaO by ball milling in benzene. The CaO was obtained from reagent $Ca(OH)_2$ per calcining Procedure A of the Appendix, as previously reported.(2)

All four specimens were fired to 1565°C per Firing Schedule A of the Appendix and three were subsequently fired along with billets cut from a MgO - 5 w/o CaO fusion to 2200 - 2400°C in an induction heated carbon furnace to improve alloy homogeniety. This latter treatment gave the specimen surfaces a black appearance from carbon contamination, even though they were placed on MgO crystals. The fused ingot billets were machined after this latter firing and were found to be blackened to a depth of only 0.1" or less.

b. MgO-ZrO_2

Several blanks for 1.5" diameter billets were cut from the MgO - 2 w/o ZrO_2 fused ingot. Two of these were machined to size, one after firing to about 2300°C. The carbon penetration in the latter was about 0.1" as with the MgO - 5 w/o CaO.

Portions of this ingot were crushed and milled for five days in a rubber lined mill. This powder was then used to make billets to eliminate the substantial gross porosity and to reduce the grain size from that of the fused ingot. Vacuum hot pressing two billets at 1620°C for 5 minutes in graphite dies with pressure being applied at about 925°C and reaching 5000 psi at about 1200°C, resulted in porosities of approximately 1.5% - substantially below that of the fused ingot. Grain size was about 25 microns after firing these billets to 1565°C in five days, as compared with grain sizes ranging from about 100 microns to over 1000 microns in the fused ingot. Lowering the hot pressing temperature to about 1510°C for a third billet increased the porosity to about 10%. However, 10% porosity appears to be abnormally high since previous fabrication of 0.25" thick disks of the same composition has resulted in porosity increasing from less than 1% to less than 2% on lowering the hot pressing temperature from 1620°C to 1565°C.

*All future alloys will be formulated on the basis of 100 parts total (e.g. 96% MgO - 4% CaO). Previously fabricated compositions based on 100 parts base material (e.g. 100 parts MgO - 4 Parts CaO) will not be distinguished since the small difference is not significant at this stage of alloy development.

Fisher MgO was mechanically mixed with colloidal ZrO_2 and hot pressed in graphite dies per vacuum hot pressing Procedure B. This billet had a porosity of less than 1%.

c. MgO-NiO

Six MgO - 2 w/o NiO were fabricated in graphite dies per vacuum hot pressing Procedure B of the Appendix except that vacuum was not used because it apparently increases reduction of the NiO as previously noted[1]. These specimens were fired with resulting densities as shown in Table I.

d. $MgO-Al_2O_3$

Ten MgO - 1 w/o Al_2O_3 billets hot pressed in graphite dies per vacuum hot pressing Procedure A of the Appendix have been fired with resultant densities as indicated in Table I.

3. ZrO_2

Samples of a partially stabilized (2.9% CaO) zirconia , Zircoa C*, were obtained and found to have 2.5% or less porosity. Billets have been ordered to accompany MgO or CaO and CeO_2 billets for a preliminary evaluation of ZrO_2 extrudability.

4. CeO_2

Preliminary investigation of techniques to fabricate CeO_2 billets were undertaken using Lindsay** 99.9+% pure, reagent grade*** CeO_2, and a mixture of rare earth oxides (Lindsay, Code 330) containing about 48% CeO_2 and stabilized in the fluorite structure[5]. Compaction curves were run on these materials in graphite dies as sketched in Figure 1. Experience with MgO has shown best results by applying pressure in the region of rapid compaction (about 675°C with LiF and 900°C without LiF). In the first pressing, Figure 1A, the rare earth mixture changed from a dark cinnamon brown to a light yellow with an apparently metallic surface. Upon subsequent air firing to 1565°C, the specimen crumbled to a powder like the starting material indicating complete reduction during hot pressing. The specimen pressed per Figure 1B showed substantially lower, but still detrimental reduction. Reagent CeO_2 pressed per Figure 1C was changed from a light pink color to black and delaminated in fine fragments

*Product of Zirconium Corporation of America
**Product of Lindsay Rare Earth Chemical
***Product of G. Frederick Smith Chemical Company

upon hot pressing. Reducing the pressing temperature to about 1000°C, 3500 psi pressure applied at about 800°C for the reagent CeO_2 resulted in a solid specimen of dark gray color. Upon firing to 1565°C, the specimen cracked and changed to a cinnamon brown. Use of a Hastalloy B die at approximately the same conditions resulted in a pink to light brown (especially near the surface) specimen. Because of thermal expansion differences, this specimen was ejected from the die in the graphite susceptor heated furnace, probably resulting in some reaction. Firing of this specimen to 1565°C increased the density from 6.4 gm/cc to 6.5 gm/cc, turned it brown, but did not show the distinct cracking of its companion specimen hot pressed in graphite.

Two specimens of CeO_2 and two of the rare earth mixture were cold pressed and fired to 1565°C. The CeO_2 was a light pink color, and the rare earth mixture was black. After firing to 1680°C, which did not appear to make any substantial changes, these specimens had densities of about 6.3 gm/cc (theoretical density is about 7.3 gm/cc).

B. EXTRUSION

Extrusions were performed by Nuclear Metals, Incorporated, Concord, Massachusetts. Selection and analysis of extrusions are made jointly by Boeing and Nuclear Metals.

1. Catch Tube

A catch tube without vacuum capabilities was designed to receive and control the cooling rate of the extrusion. It is felt that slower cooling between 2000° and 300°C may substantially reduce or eliminate cracking. Initially, MgO powder insulation was used; however, a trial extrusion with a molybdenum alloy (TZM) billet resulted in a tube being pulled away from the press. Carbon felt insulation was then evaluated, but this was dislogded by a bare extruded billet. Graphite sections have now been prepared for trial as insulation in the tube.

2. Bare Extrusion

It was decided that a metal nose consisting of molybdenum alloy (TZM) would aid initiation of extrusion of the large uncanned MgO billets and that a copper cylinder on the tail of the MgO would allow complete extrusion of the billet. A wrapping of 5 mil tantalum foil was used to prevent a carbon-molybdenum eutectic and to hold the nose, billet and cut-off together. Some radiation shielding to limit cooling during transfer between the carbon heated furnace and the extrusion press is also obtained.

A trial with a TZM dummy in place of the MgO revealed the need for better alignment of the press loading chute to allow better transfer of the billet from the heating furnaces. This was corrected and a graphite sleeve with 0.1" thick walls was added to improve lubrication. A second composite billet with a TZM dummy and this modification was again heated to 4000°F (2200°C) and a completely successful extrusion was achieved.

These techniques were then applied to MgO, except a TZM tail was used, and a layer of molybdenum foil* was placed between the tantalum and MgO to prevent possible reaction. This billet was temporarily stalled in the loading chute as was the first dummy above. By the time it was successfully loaded in the press substantial cooling had occurred, much of the MgO fell away as the ram pushed it in the press liner, and the remainder of the billet stalled in extrusion. A second billet was prepared with two layers of molybdenum foil to provide greater strength and prevent partial separation of the components observed in the previous extrusion attempt. This composite billet also became temporarily lodged in the loading chute, but was then successfully loaded in the press liner. This extrusion also stalled, apparently due to excessive cooling during the delayed loading and to a forward displacement of the thin wall graphite sleeve that was used for lubrication as described above. However, some back extrusion of the MgO billet around the ram, apparently due to the forward displacement of the graphite sleeve, indicated encouraging plasticity.

The loading chute alignment and lubrication were again improved and checked by the successful loading of another TZM dummy. Another composite billet consisting of a TZM nose and tail and a 3.0" diameter MgO billet also held together by two layers of 5 mil molybdenum foil and one of tantalum were heated to 4000°F (2200°C). This was successfully loaded in the press liner with the 0.1" thick wall graphite lubricating sleeve and was successfully extruded. However, pressure gauges showed that the MgO extruded with varying pressure in contrast to the smoothly extruding TZM nose and tail, indicating fragmentation of the MgO during extrusion. Inspection of the extruded material (which had dislodged the carbon felt in the catch tube) verified the fragmentation of the MgO.

3. Canned Extrusions

Delivery of necessary tungsten cans took over a month longer than normal and correspondingly delayed further canned extrusions. However, the cans were recently received, machined, loaded, and welded closed

*Due to the use of the foil and the lubricating graphite sleeve, these are not true "bare" extrusions and are better termed uncanned extrusions.

and three extrusions have just been successfully completed.

C. MATERIAL ANALYSIS

1. Analysis of Preferred Orientation

A(200)pole figure previously obtained[3] for MgO extruded at approximately 2150°C is shown in Figure 2. The (200)pole figure for a CaO billet (No. 8) extruded at 2000°C is shown in Figure 3. The two pole figures are quite similar, as expected, especially when it is noted that:

a. Symmetry of the horizontal central bands depends on how close the longitudinal section is to being parallel to the extrusion axis.

b. Uniformity of the bands depends on how close the longitudinal section is to the extrusion axis.

c. Effort to obtain close tolerances for proximity and parallelness to the extrusion axis was not deemed warranted.

With the pole figure of a base material such as MgO as a reference the angular variations of the intensity of the selected crystallographic plane relative to the extrusion axis are then compared for further extrusions of that material or its alloys. This is shown in Figure 4A and B for MgO bodies extruded to date and for MgO - 2 w/o NiO and MgO - 1 w/o Al_2O_3 in Figure 4C and D. A shift of the peak maximum from zero is due primarily to variations of the transverse section from prependicularity with the extrusion axis either due to some bending of the extrusion, or inaccuracy in the cutting of a perfect transverse section and also possibly due to asymmetrical cracking. The asymmetry of the fused MgO extrusion is believed to be due to the mixed grain structure before and after extrusion[1]. Some asymmetry is probably carried over from the large columnar grains of the original fused ingot. The hump and asymmetry of the MgO - 1 w/o Al_2O_3 curve is believed due to asymmetrical longitudinal cracking found in this transverse section. Comparison of the orientation of two extrusions must take into account the relative grain sizes and extrusion reduction ratios, as well as the above factors. Evaluation of all of these factors indicates that the MgO - 1 w/o Al_2O_3 has substantially higher orientation, and MgO - 2 w/o NiO somewhat higher orientation than similarly extruded polycrystalline MgO.

The X-ray data also showed a decrease in lattice parameter from 2.019Å to about 2.083Å for the MgO - 2 w/o NiO extrusion, indicating solid solution.

2. Alloy Analysis

Electron probe analysis showed general dispersion of the NiO in the MgO-2w/o NiO extrusion, in agreement with the above X-ray data showing general solid solution.

As previously reported[4], the MgO-5w/o CaO fusion consisted mostly of equiaxed grains averaging about 1 mm in diameter with a radial section of columnar grains about 4 mm long by about 1 mm in diameter. One to two per cent CaO was dissolved in the MgO rich grains which contained a few large precipitates of a CaO phase with 1-2% MgO in solid solution. This latter phase also surrounded all grains and only began to dissolve at temperatures above 2000°C, disappearing last from the triple lines. This is indicated in Figure 5A. Examination showed that extrusion in general reduced both the width and continuity of this CaO rich phase and that precipitation occurred along part of some of the new grain boundaries formed. This is shown in Figure 5B, where a remnant outline of one columnar grain is also seen.

The fused CaO - 14 w/o MgO ingot consisted of grains 50 to 200 microns in diameter. The ingot was generally characterized by three regions: 1) MgO rich grains with a CaO rich phase surrounding them and forming some precipitates in them, 2) CaO rich grains with a MgO rich phase surrounding them and forming some precipitates in them, and 3) an eutectic-type structure[4]. Examples of the first two regions are shown in Figure 6A and B, respectively in a sample briefly heated to about 2100°C (to duplicate extrusion heating), which did not change the structure. No significant changes in alloy distribution were observed on extrusion as shown in Figure 6C and D. However, Figure 6C and D suggest a possible orientation of the alloy structure. Figure 7 reveals the phases by surface relief. This shows much the same effect; however, since these photos are not completely typical, they probably give an indication of greater orientation than the average.

3. Recrystallization

Closer examination of CaO billet number 8[1] after extrusion indicated some highly elongated grains as shown in Figure 8. (The general intergranular fracturing and the somewhat larger grain size seen in Figure 8 are in agreement with previous observations of cracking in extruded CaO and of a secondary effect of starting grain size.)[1] This indicates that substantial grain elongation occurs during extrusion and that this is generally lost, at least in unalloyed bodies due to partial recrystallization.

As shown previously[1] and seen in Figure 9A the extruded CaO is quite nonequiaxial in grain structure indicating only partial recrystallization and in agreement with other hot extrusion analysis.[3] However, as shown in Figure 9B and C,no change is noted in firing to 1100°C or 1370°C. This is in contrast to data showing that hot extruded MgO recrystallized between 1050°C and 1200°C, especially when it is recalled that CaO would be expected to recrystallize at a lower temperature than MgO because of its lower melting temperature.

DISCUSSION AND CONCLUSIONS

Fabrication of MgO billets without LIF per vacuum hot pressing Procedure B of the Appendix will now be the primary fabrication technique because:

1. Densities almost, if not as high as, those achieved with LIF can be obtained.

2. It is a faster and cheaper method due to the elimination of mixing, milling and drying required with LIF.

3. It eliminates any question of residual fluorides.

4. Comparable or greater strengths than achieved with LIF have been achieved in other studies at Boeing

Fisher MgO has been selected as the best material for this process because it showed less blistering and indicated a lower impurity content in billet fabrication. This is in agreement with earlier studies on thin specimens at Boeing, where Fisher MgO also yielded lower porosities than the Mallinckrodt MgO.

Firing to 1565°C per firing Schedule A of the Appendix has been made the basic firing procedure because it:

1. Reduces contaminates in MgO billets made without LIF.

2. Reduces fluoride contaminates left from the use of LIF as shown in other studies at Boeing.

3. Improves alloy distribution.

4. Reoxidizes NIO in alloy bodies as indicated by color changes.[1]

Increasing the pressing temperature to 1900°C made large improvements in the densities of 3.0" diameter billets, though some reaction with and bonding to the die was encountered. This bonding can probably be reduced or eliminated by the use of graphite cloth. Use of finer grain may yield further density increases without substantial increase in the volume of powder required.

Hot pressing CeO_2 at temperatures as low at 1000°C apparently results in substantial reduction of the material, probably to Ce_2O_3. Since there is apparently extensive reduction of the pink CeO_2 on hot pressing, especially in graphite dies and Ce_2O_3 is gray to green in color, it is suggested that the brown color after firing to 1565°C is due to a mixture of Ce_2O_3 and CeO_2. This would mean that rather incomplete

reoxidation occurs in air at that temperature. The improvement in the CeO_2 hot pressed in the Hastalloy B die heated by a graphite susceptor indicates that hot pressing in this die in an oxidizing atmosphere may be successful. The preliminary cold pressing trials indicate that isostatic pressing and firing may also produce good billets.

Canned extrusion has been selected as the primary extrusion method for the remainder of this program because:

1. Further development of uncanned techniques is required.

2. Greater fabrication problems and costs combined with lower quality for the larger billets would not allow the scope of investigation that may be conducted with smaller billets used in canned extrusion at this stage of development.

3. The present stage of development indicates it would be difficult, if not impossible to make tandem extrusions of several uncanned ceramic billets.

The back extrusion of MgO, and the final successful uncanned extrusion, though with extensive fragmentation, indicates that further development would be successful. Such development would be valuable in understanding extrusion behavior, would probably make reductions in overall extrusion costs and allow a greater volume of extruded material. Further uncanned extrusions will be attempted as is found feasible.

Analysis shows substantial interaction between alloying and extrusion in the favorable redistribution of alloy agents observed in MgO-5w/o CaO and indicated in CaO-14w/o NiO.

Recrystallization during cooling from extrusion is indicated in CaO, as would be expected for any extrusion, at least without alloying effects. However, this partial recrystallization can result in a finer than starting grain size[1] and apparently does not reduce the orientation effects of extrusion.[3] The lack of further recrystallization upon annealing of extruded CaO with nonequiaxed grains is, however, as yet unexplained.

WORK IN PROGRESS AND PLANNED

CeO_2 billets will be fabricated probably by isostatic pressing. These will be combined with the ordered ZrO_2 billets in future extrusions of CaO or MgO.

At least one more uncanned extrusion experiment will be performed. Further development of this technique will be considered, possibly using fused billets if suitably large ingots can be obtained.

Further canned extrusions will be initiated as soon as the latest series of extrusions can be surveyed for selection of parameters. Evaluation of extrusion and alloy effects will be performed on these extrusions.

Errata: Figures 6 and 7, but not the captions, were interchanged in the last report.[1]

REFERENCES

(1) Progress Report 1, "Identifying Optimum Parameters of Hot Extrusions", Contract NAS 7-276, April 17 to July 13, 1964.

(2) R. W. Rice, "Fabrication of Dense CaO", Presented at the 65th Annual American Ceramic Society Meeting in Pittsburgh, Pennsylvania, April 1963.

(3) R. W. Rice, J. G. Hunt, "Hot Extrusion of MgO", Presented at the 66th Annual American Ceramic Society Meeting in Chicago, Ill., April 1964.

(4) R. W. Rice, "Ceramic Alloying", Presented at the 66th Annual American Ceramic Society Meeting in Chicago, Ill., April 1964.

(5) Private Communication with Howard Kremers (Representing Lindsay Rare Earth Chemical) who Kindly Supplied this Material.

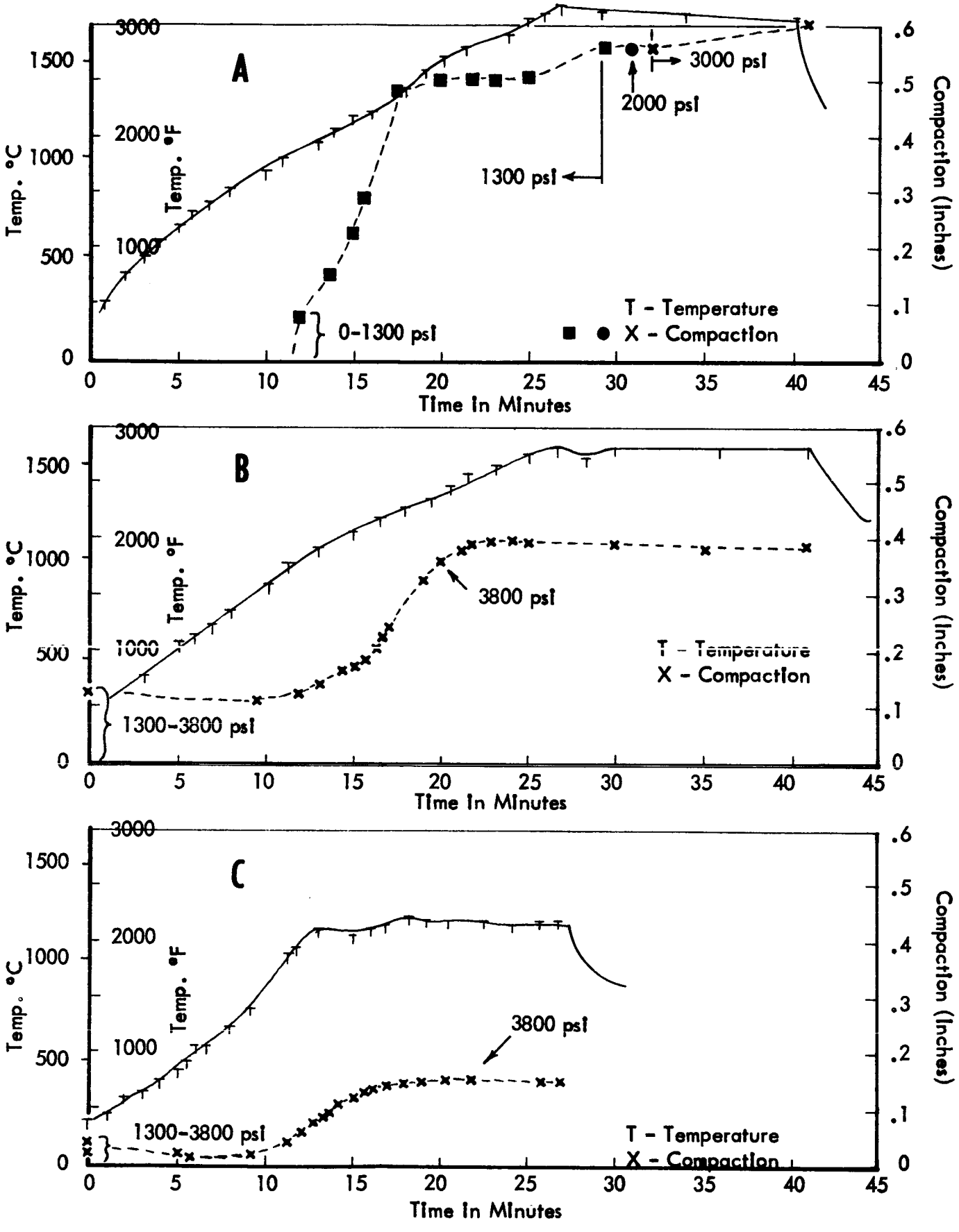
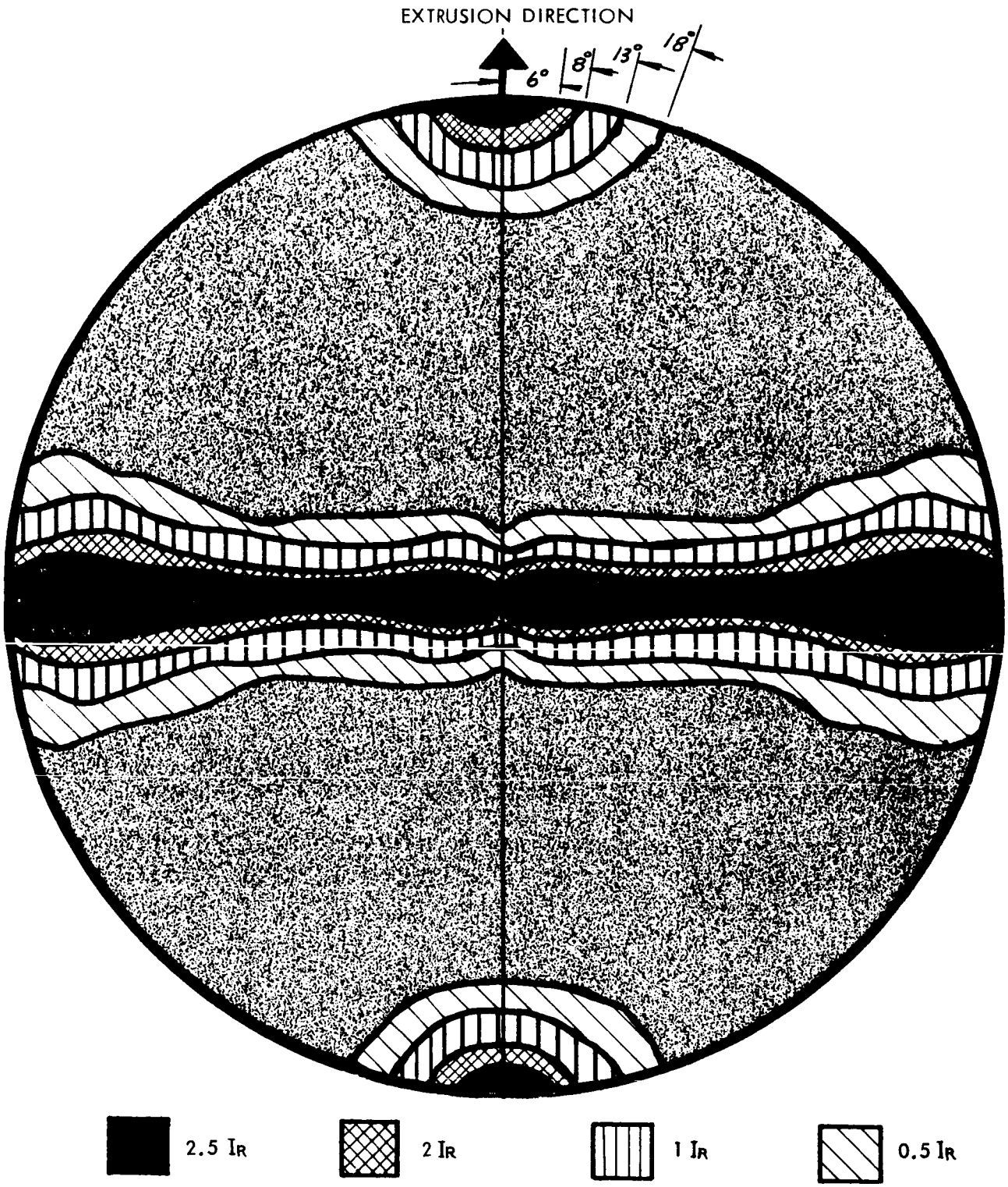


FIGURE 1 COMPACTION CURVES OF MIXED RARE EARTH OXIDES, PRIMARILY CeO_2 (A AND B) AND REAGENT CeO_2 (C)

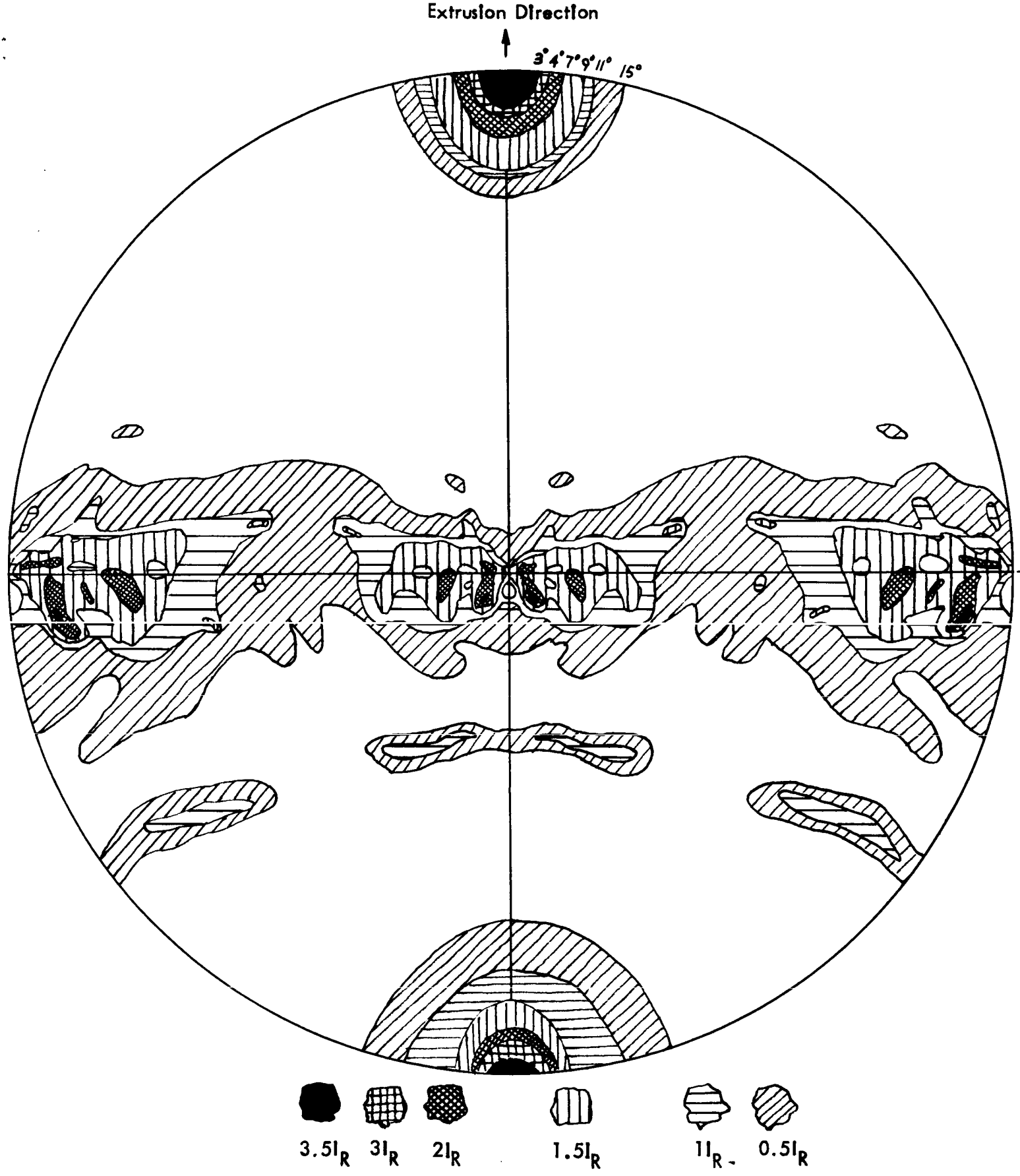
SOLID MgO BILLET EXTRUDED AT 2150°C



I_R = INTENSITY OF RANDOMLY ORIENTED SAMPLE

(002) [001] TEXTURE

FIGURE 2 (200) POLE FIGURE OF EXTRUDED MgO



I_R = Intensity of Randomly Oriented Sample

FIGURE 3 (200) POLE FIGURE OF EXTRUDED CALCIUM OXIDE. DATA AVERAGED ABOUT EXTRUSION AXIS. ANGLES AT TOP ARE APPROXIMATE ANGLES FROM EXTRUSION AXIS FOR THE NOTED INTENSITY

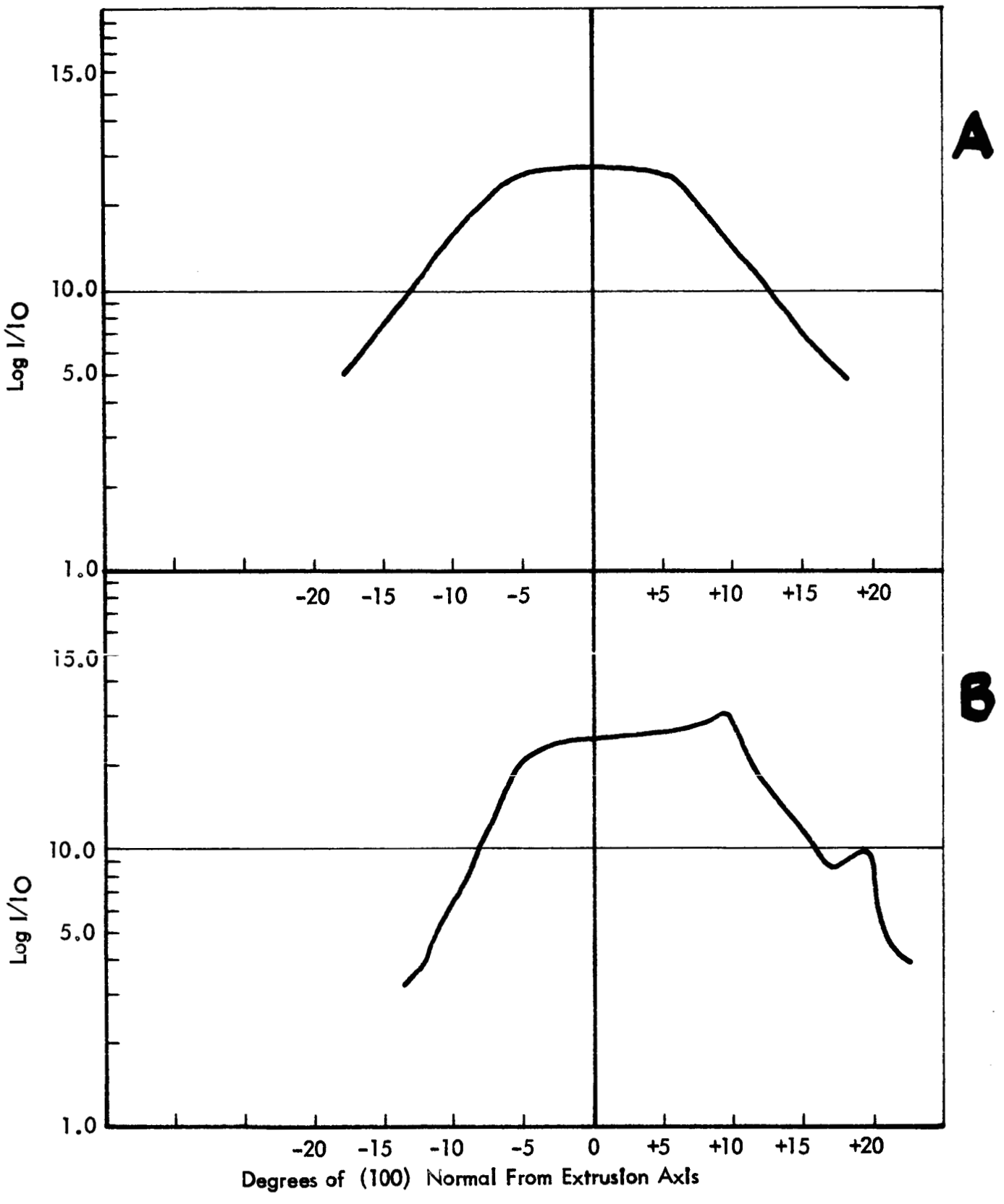


FIGURE 4 EXTRUSION ORIENTATION. THE INTENSITY I, OF THE (100) PLANE FOR AN EXTRUDED BILLET RELATIVE TO THE INTENSITY, I_O, OF A RANDOM SAMPLE IS PLOTTED VERSUS THE ANGULAR DEVIATION OF THE (100) PLANE'S NORMAL RELATIVE TO THE EXTRUSION AXIS. A) POLYCRYSTALLINE MgO. B) FUSED MgO CRYSTALS (APPROXIMATELY 3 COLUMNAR CRYSTALS).

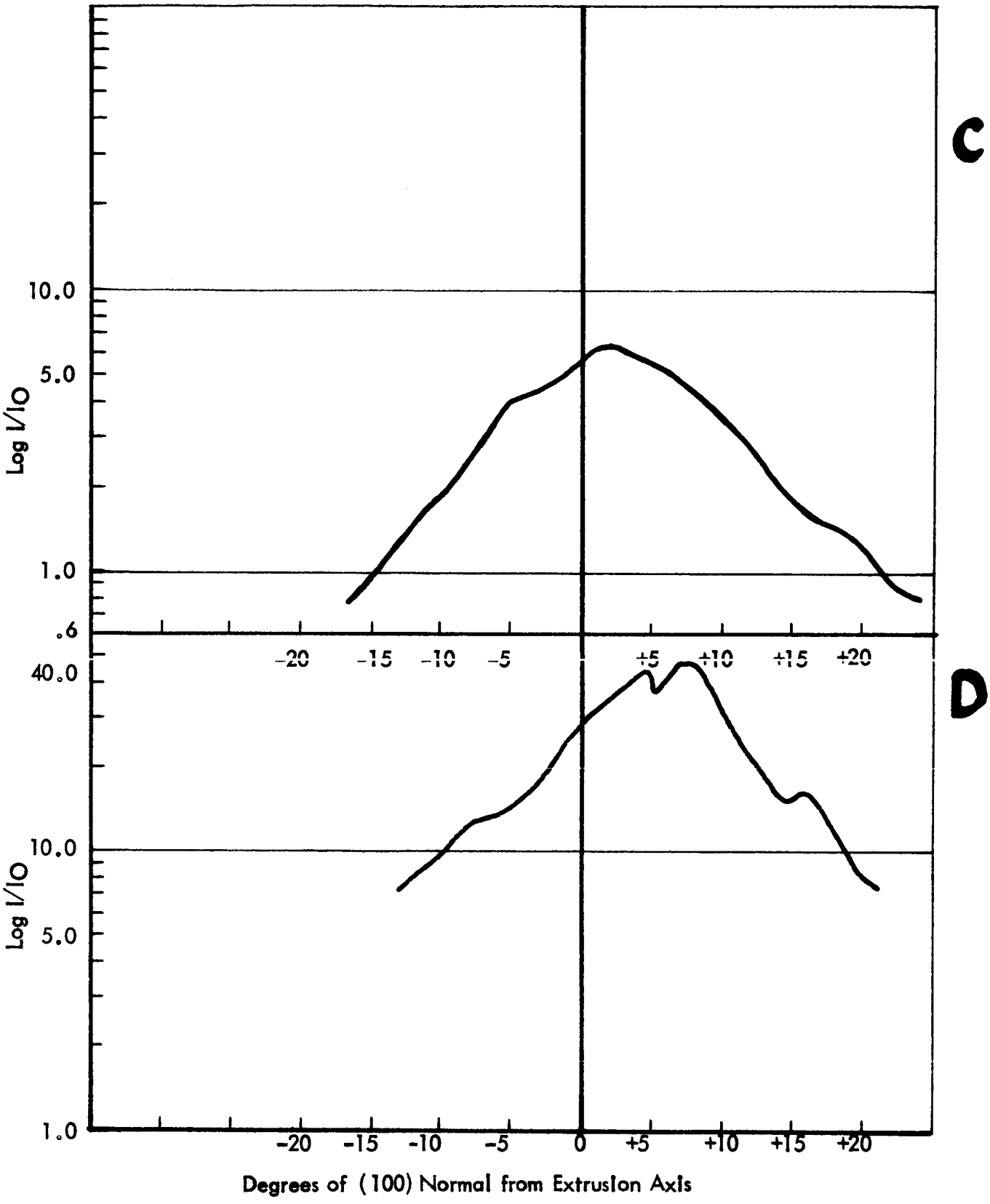


FIGURE 4 (CONTINUED) C) MgO - 2 w/o NiO. D) MgO - 1 w/o Al_2O_3
ALL EXTRUDED AT 2150°C

A

45 μ

B

EXTRUSION DIRECTION →

FIGURE 5 MgO-5 W/O CaO FUSION. PROBE ELECTRON BACK SCATTER ANALYSIS: BRIGHT WHITE-CaO RICH, GRAY-MgO RICH, BLACK, VOID, CRACK, OR GRAIN PULL-OUT. (A) TYPICAL CaO AND MgO DISTRIBUTION AS FIRED TO ABOUT 2200°C BEFORE EXTRUSION, (B) AFTER EXTRUSION

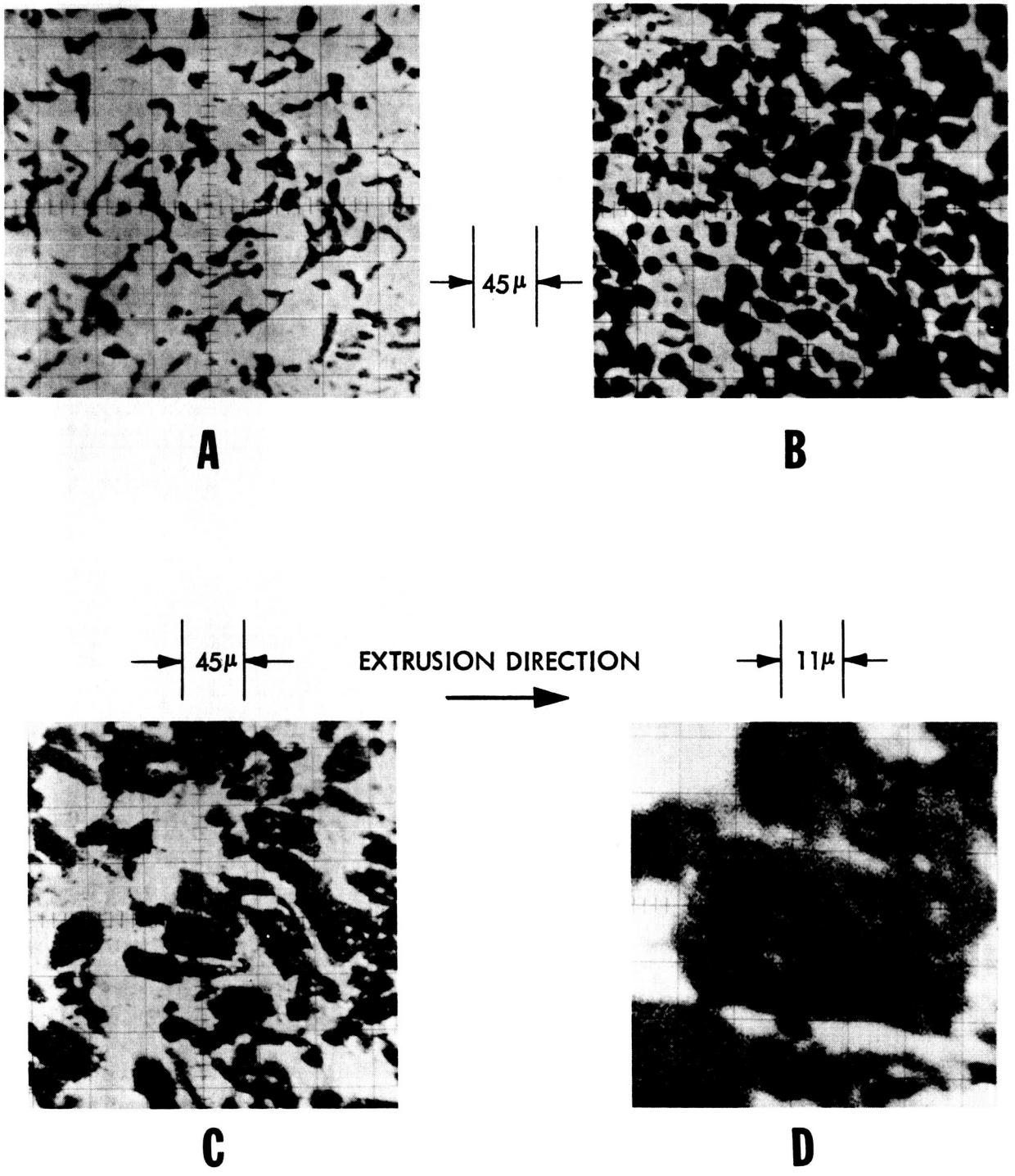


FIG. 6 ELECTRON PROBE ANALYSIS OF FUSED CaO- 14 w/o MgO BRIGHT WHITE - CaO RICH, GRAY TO BLACK - MgO RICH. (A) AND (B) SAMPLE QUENCHED FROM 2100°C. (C) AND (D) AFTER EXTRUSION

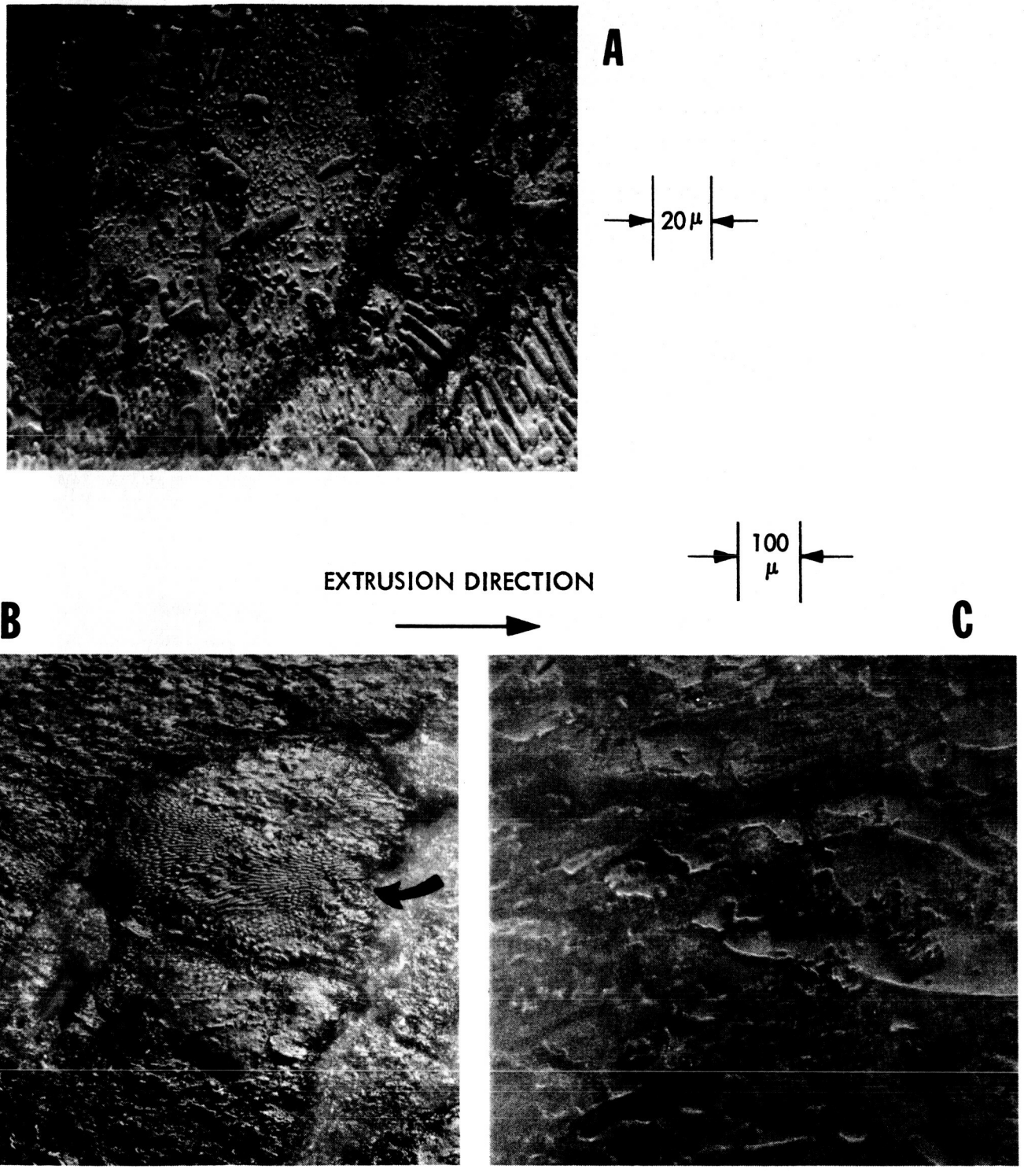


FIG. 7 FUSED CaO-14 w/o MgO AFTER EXTRUSION, (A) TRANSVERSE SECTION. (B) AND (C) LONGITUDINAL SECTION. NOTE ARROW INDICATING PROBABLE EUTECTIC STRUCTURE

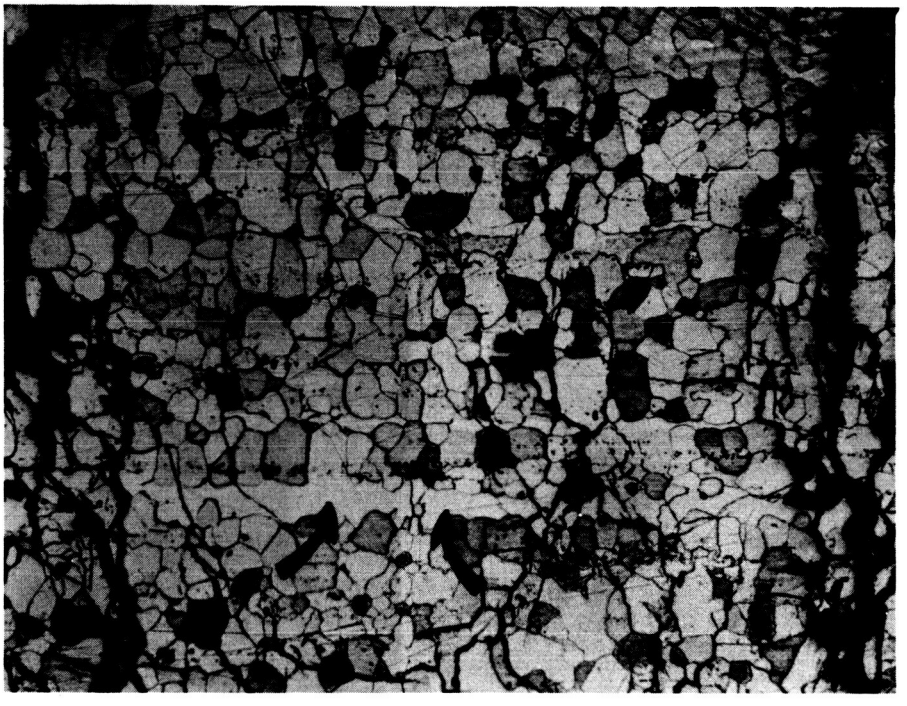


FIGURE 8 CaO BILLET NO. 8, AS EXTRUDED LONGITUDINAL SECTION. NOTE ARROWS INDICATING ELONGATED GRAINS.

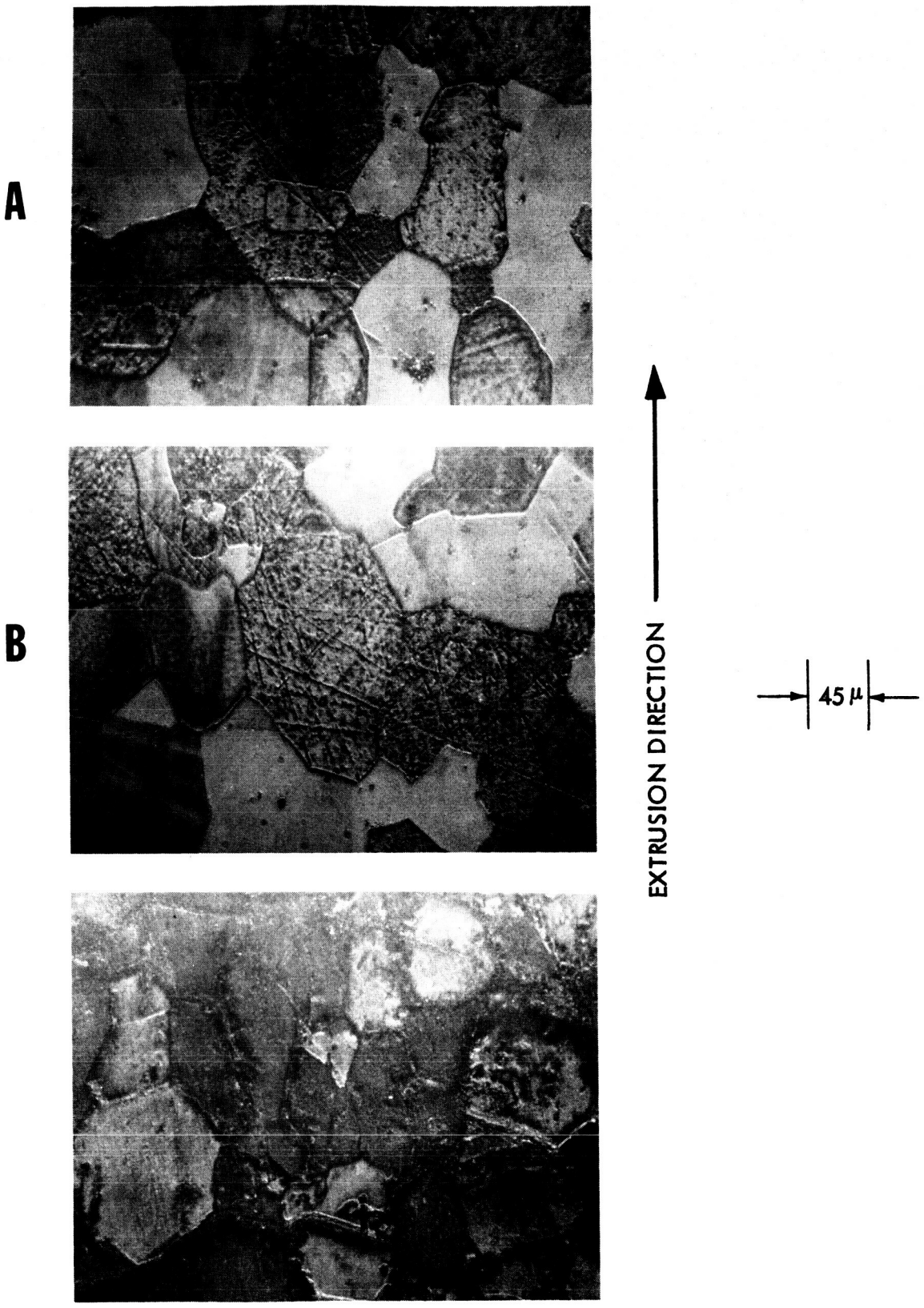


FIGURE 9 CaO BILLET NO. 9, LONGITUDINAL SECTION, A. AS EXTRUDED, B. FIRED TO 1100°C (2010°F) FOR 1 HOUR, C. FIRED TO 1370°C (2500°F) FOR 1 HOUR

TABLE I BILLET FABRICATION

Billet Number	Composition	Fabrication	Firing Schedule	Density gm/cc[1]
M-f-3	MgO	Fusion		3.57
M-f-4				3.58
M-f-5				3.58
M-1-1	Mallinckrodt MgO	Per Vacuum Hot Pressing Procedure A	A to 1315°C(2400°F)	
M-1-2			A to 1380°C(2525°F)	
M-1-3			A to 1315°C(2400°F)	3.57
M-1-4			A to 1380°C(2525°F)	3.26
M-1-5			A to 1565°C(2850°F)	3.52
M-1-6			↓	3.54
M-1-7			↓	3.55
M-1-8			↓	3.53
M-1-9	Mallinckrodt MgO	Per Vacuum Hot Pressing Procedure B	A to 1565°C(2850°F)	
M-1-10			↓	3.53
M-1-11			↓	3.54
M-1-12			↓	3.56
M-1-13	Fisher MgO		↓	3.55
M-1-14			↓	3.45
M-1-15			↓	3.45
M-1-16			↓	3.54
M-1-17			↓	3.54
M-1-18			↓	

TABLE I (CONTINUED)

Billet Number	Composition	Fabrication	Firing Schedule	Density gm/cc[1]
M1A-1-2			A to 1315°C(2400°F)	
M1A-1-3			A to 1380°C(2525°F)	
M1A-1-4		Per Vacuum	A to 1315°C(2400°F)	3.57
M1A-1-5	MgO - 1 w/o Al_2O_3	Hot Pressing		3.55
M1A-1-6		Procedure A		3.56
M1A-1-7			A to 1565°C(2850°F)	3.49
M1A-1-8			A to 1565°C(2850°F)	3.53
M1A-1-9			A to 1380°C(2525°F)	3.50
M1A-1-10			A to 1380°C(2525°F)	3.53
M1A-1-11			A to 1565°C(2850°F)	
M2N-1-1			A to 1565°C(2850°F)	
M2N-1-2		Vacuum Hot		
M2N-1-3		Pressing Procedure		3.40
M2N-1-4	MgO - 2 w/oNIO	A, Except Vacuum		3.47
M2N-1-5		Not Used		
M2N-1-6				
M2N-1-7				3.36
M2N-1-8				3.37
M10N-1-1	MgO - 10w/o NiO	Fusion	-	-
M4C-1-1		Per Vacuum	A to 1565°C(2850°F)[2]	3.37
M4C-1-2	MgO - 4w/o CaO	Hot Pressing		
M4C-1-3		Procedure B		
M4C-1-4				3.43
M5C-1-2	MgO - 5w/o CaO	Fusion	Fired to Apprx. 2300°C	3.45[3]
M5C-1-3				

TABLE I (CONTINUED)

Billet Number	Composition	Fabrication	Firing Schedule	Density gm/cc[1]
M2Z-1-1	MgO-2 w/o ZrO_2	Fusion	Fired to 2300°C A to 1565°C(2850°F) ↓	
M2Z-1-2				
M2Z-1-3		Hot Pressed as Described In Text		3.55
M2Z-1-4				3.56
M2Z-1-5				3.26

[1]Nominal density error is ±.01 gm/cc.

[2]Subsequently fired to approximately 2300°C. Densities are after final firing.

[3]Large surface pores not reflected in this Figure.

APPENDIX
CALCINING PROCEDURE A

1. Powder is loaded in 99% pure MgO crucibles approximately 3" in diameter by 4" high with 0.1" wall thickness by using the crucible to scoop powder from the container.

2. The crucibles are placed in a metal retort with half of them inverted on top of the remainder. The top crucibles are slotted on the side near their base to allow ready gas escape and good flushing while acting as lids to prevent excess spillage of powder, and possible contamination from the retort metal lid.

3. A thin metal lid is welded on the retort to seal it.

4. Lines are attached to fittings to introduce argon at the bottom in front, and a vacuum system to the top of the retort in the back.

5. The retort is loaded in the furnace and the vacuum and argon valves are set to establish an argon flush at about 10" absolute pressure.

6. The retort is heated at a linear rate to reach 600°C (1110°F) in approximately 5.5 hours. Temperatures are measured by a thermocouple near the center of the retort.

7. After 1 hour at 600°C, the retort is cooled in approximately 1.5 hours, initially in the furnace, then out of the furnace.

8. When the retort is less than 100°C the vacuum valve is closed, when the retort is near atmosphere pressure, the argon valve is closed, and the retort is flooded with benzene through a third fitting.

9. The thin retort lid is then removed and the powder, covered with benzene, is transferred to jars which are closed for storage.

APPENDIX
BILLET VACUUM HOT PRESSING PROCEDURE A (WITH LIF)

1. Two weight per cent reagent grade LIF is added to the ceramic powder by milling for 2 hours in an organic fluid, normally benzene.

2. The milled slurry is dried, screened through a number 28 screen, and stored in sealed jars. The time of storage in sealed jars is normally less than one week prior to complete usage of the powder.

3. Powder is loaded in the die by cold pressing at 1000-2000 psi. Pyrolytic graphite spacers are placed between the rams and the powder when graphite dies are used.

4. The die is placed in the vacuum hot press which is pumped down to a chamber pressure of 10^{-4} - 10^{-5} Torr in about 1 hour.

5. After at least 4 hours at 10^{-4} - 10^{-5} Torr, the die is heated at an approximately linear rate to 650°C (1200°F) in about 0.5 hours. Temperatures are measured by a thermocouple in the die wall approximately 0.75" from the inside die surface and about 1" above the specimen.

6. Between 650°C and 700°C the ram pressure is built up to approximately 3500 psi.

7. Heating, while maintaining this ram pressure, is continued at a slightly slower rate until a temperature of 980°C (1800°F) is reached after a total heating time of 50 to 60 minutes.

8. Pressing conditions of 980°C and 3500 psi are held for 15 minutes with vacuum chamber pressure averaging 2 to 4 x 10^{-3} Torr.

9. The heating power is shut off and the ram pressure released over a period of about 1 minute.

10. The die is removed from the vacuum hot press after 2 to 4 hours of cooling.

11. The specimen is ejected from the die at temperatures of 400°C or less.

APPENDIX
BILLET VACUUM HOT PRESSING PROCEDURE B (WITHOUT LIF)

1. Powder is directly loaded into the die from sealed bottles, without any prior milling unless milling was previously used to mix alloy agents. Pyrolytic graphite spacers are used between the rams and the specimen when graphite dies are used.

2. The powder is cold pressed at 1000-2000 psi.

3. The die is placed in the vacuum hot press which is pumped down to a chamber pressure of 10^{-4} to 10^{-5} Torr in about one hour.

4. After at least 6 hours at 10^{-4} - 10^{-5} Torr the die is heated to 900°C (1650°F) in about 30 minutes. Temperatures are measured by a thermocouple located in the die wall about 0.75" from the inside die surface and about 1" above the specimen.

5. Starting at 900°C the ram pressure is built up to 5000 psi over a period of about 2 minutes.

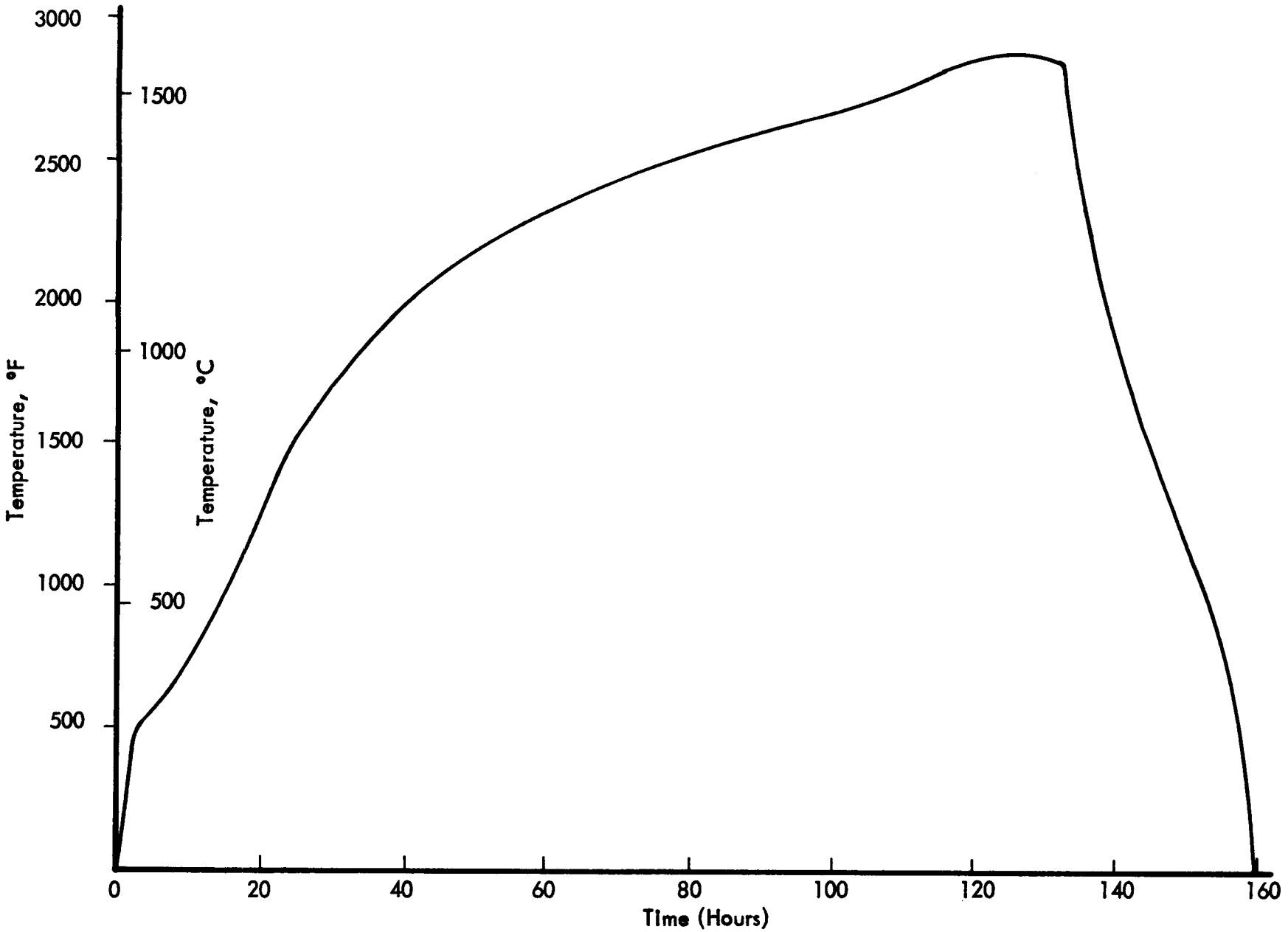
6. A temperature of 1205°C (2200°F) is then reached in about 20 minutes, while maintaining the ram pressure at 5000 psi.

7. Pressing conditions of 1205°C and 5000 psi are held for 15 minutes with vacuum chamber pressure averaging about 10^{-2} Torr.

8. The induction heating power is shut off and the ram pressure released over a period of about 1 minute.

9. The die is removed from the vacuum hot press after cooling for two to four hours.

10. The specimen is ejected from the die at a temperature of 400°C or less.



FIRING SCHEDULE A

APPENDIX
TABLE I
INITIAL 3.0" DIAMETER MgO BILLETS

Screen Size or Powder Source	% Powder Composition of Grain Size							Mallinckrodt A. R. Powder
	+14	-14 +20	-20 +28	-28 +65	-65 +200	-200 +325	-325	
Billet	← Norton Fused MgO →							
A	-	43	-	19	-	19	15.5	3.5
B	-	43	-	19	-	19	15.5	3.5
1	-	35	-	20	-	20	15.0	10 wt % LIF
2	-	30	-	5	30	5	15.0	15 wt % LIF
3	-	30	-	5	30	5	15.0	15 wt % LIF
4	10	-	20	5	30	5	15.0	15 No LIF

Fabrication and Results

		Final Density
A	Cold pressed - fired to 1540°C in 3 days	2.59 gm/cc
B	Rammed - fired to 1540°C in 3 days	2.57 gm/cc
1	Rammed in graphite die	2.38 gm/cc
	Vacuum hot pressed at 10^{-3} Torr, 1205°C, 1500 psi	2.70 gm/cc
	Fired to 1540°C in 6 days	2.80 gm/cc
2	Cold pressed in die - vacuum hot pressed at 1370°C, 2×10^{-2} Torr, 1500 psi	2.88 gm/cc
	Fired to 1540°C in 6 days	2.92 gm/cc
3	Same as 2 except hot pressed at 1620°C, 2000 psi, fired same as 2	2.97 gm/cc
4	Same as 2 except hot pressed at 1600°C, 2000 psi, fired same as 2	2.95 gm/cc